Colloids and Surfaces B: Biointerfaces 171 (2018) 167–175

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Detailed characterization of POSS-poly(ethylene glycol) interaction with model phospholipid membrane at the air/water interface

Marta Skrzypiec, Krystyna Prochaska*

Institute of Chemical Technology and Engineering, Poznan University of Technology, Poland

ARTICLE INFO

Keywords:
Key words
Phospholipid (DMPE)
Polyhedral oligomeric silsesquioxanes (POSS)
Phospholipid-POSS interactions
Langmuir monolayer
Binary mixtures
Miscibility
Thermodynamic analysis

ABSTRACT

Polyhedral oligomeric silsesquioxanes (POSS) derivatives have been receiving remarkable attention due to their potential biomedical application and therefore understanding molecular mechanism of their interaction with cell membranes should be studied at molecular level. Here we investigate the binary mixture of an open silsesquioxane cage POSS-poly(ethylene glycol) (POSS-PEG) and 1,2-myristoyl-sn-glycero-3-phosphoethanolamine (DMPE) as a representative of phospholipid located in biological membranes. The surface pressure-area and surface potential-area compression isotherms, as well as Brewster angle microscopy and interfacial shear rheology were used to study monolayers at the air/water interface. The results show that POSS-PEG exhibits an insoluble monolayer with side group chains anchored to the air/water interface. The outcomes of the conducted experiments show (i) the evidence of a stable incorporation of POSS molecule to the DMPE monolayer modifying its equilibrium and dynamic properties and (ii) squeezing the POSS-polymer out of the lipid monolayer at a higher molecular packing density. The results from the conducted experiments together with thermodynamic analysis suggest area condensation and mutual miscibility at the surface pressure relevant to a real biological membrane.

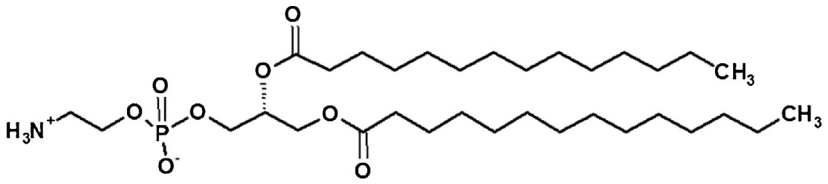
1. Introduction

The advanced progress in manipulating materials down to atomic and molecular scale have permitted a rapidly growing research in use of nanomaterials (NMs)considering their widespread applications within various scientific disciplines. Nanomaterials are usually considered to be materials of which at least one dimension (length, width or thickness) is in the 1–100 nm range [1]. Due to their nanometric size, nanomaterials generally exhibit enhanced physical, chemical and mechanical properties, such as unique optical, thermal, electrical, magnetic, catalytic characteristics compared to their non-nano counterparts [2–10]. Particularly high expectations are placed on these materials in biomedicine including cell labelling [11], antimicrobial wound dressing [12], genomics, proteomics [13], diagnostic and bioimaging tools [14], targeted drug delivery to tissues affected by diseases [15,16], production of endoprostheses and bone reconstruction in orthopaedics [17]. Nanomaterials can be used directly or indirectly by being incorporated into polymeric matrix to create nanocomposite materials. Among the different studied nanofillers or monomers for developing nanocomposite materials, silsesquioxanes play an interesting role.

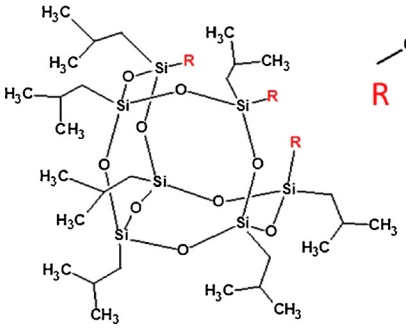
Polyhedral oligomeric silsesquioxanes (POSS) are nanostructured, hybrid inorganic/organic materials consisting of silicon and oxygen atoms linked together in a cubic core, usually functionalized with reactive or unreactive organic chains groups attached to the corners of the cage, which can be exploited to anchor different functionalities [18]. It has been found in a significant number of studies that POSS incorporation into polymers can enhance thermal stability and mechanical properties significantly [19–21]. Furthermore good biocompatibility, non–toxicity, inert nature and cytocompatibility, oxidation resistance, oxygen permeability, reduced flammability and reduced inflammatory reactions make POSS a suitable material for a cell culture and potential biomedical applications [22–24]. For instance, POSS–poly (carbonate urea) urethane (POSS-PCU) nanocomposite has been synthesized for use in a wide range of surgical implants, such as word's first synthetic trachea [25], lacrimal duct conduits [26], and lower limb bypass grafts [27]. Their anti-thrombogenic and viscoelastic properties similar to the native vessels make POSS-PCU an ideal candidate for the application of devices in contact with blood. Pu et al. [28] evaluated the drug release efficiency and anticancer activity of micelles formed by star shaped poly(L-aspartate)-b-poly(ethylene glycol) copolymers with POSS cores. Kim et al. [24] showed the improved biocompatibility of the composites of a reinforced acrylic-based hybrid denture composite resin with POSS.

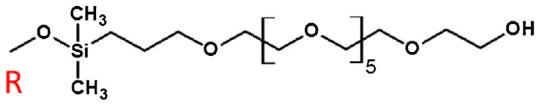
* Corresponding author at: Institute of Chemical Technology and Engineering, Poznan University of Technology, Berdychowo street 4, 60-965 Poznan, Poland.
E-mail address: krystyna.prochaska@put.poznan.pl (K. Prochaska).

https://doi.org/10.1016/j.colsurfb.2018.07.029
Received 20 April 2018; Received in revised form 23 June 2018; Accepted 13 July 2018



1,2-Dimyristoyl-sn-glycero-3-phosphoethanolamine
DMPE





3,7,14-tris{[ω-(hydroxy)(polyethoxy)propyl]di-methylsiloxy}-
1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.^{15,11}]heptasiloxane
POSS-PEG

Fig. 1. Chemical structure of studied compounds.

The discovery of the superior properties of POSS nanomaterials opens broad possibilities for numerous applications; however, it also requires comprehensive research, understanding the properties of nanoparticles and their effect on the body for twofold reasons: i) it is crucial in proper effect of many applications like phototherapy or drug/gene delivery and ii) to ensure they are safe to use [29,30]. The chances of inserting NMs into the human body are possible through a number of pathways like skin absorption [31–33], respiratory system [34], intravenous injection [35] or implantation [36]. Nanomaterials can widely interact in the physiological environment and induce a series of complicated reactions by crossing the biomembrane barrier (e.g., skin, lung surfactant, intestinal barrier or cell membrane), therefore it is of great scientific importance to understand the underlying mechanism of the interaction of nanomaterials with cells and lipid bilayers. The lipid membranes are of highly complex structures, hence their biophysical interactions with nanomaterials are difficult to investigate. Therefore the simplified artificial membranes systems mimicking the real lipid membranes have been developed. Among various systems to mimic biological phenomena, Langmuir monolayers have extensively been used as a simple model to understand interactions at the molecular level [37].

This study presents the results for POSS-PEG, containing incompletely condensed silsesquioxane cage coupled with three hydrophilic, polyethylene glycol (PEG) functional groups. Regarding biomedical aspects, PEG is known to reduce cytotoxicity [38], to be biocompatible [39], non-immunogenic and non-antigenic [40]. Poly (ethylene glycol) has been widely studied and applied in many technological fields like tissue engineering, drug delivery or in the reticuloendothelial system (RES) [41]. Thus, it is not surprising that POSS-PEG have been found to be a good candidate for wound closure with strong adhesion and good biocompatibility [42] or cartilage tissue engineering [43]. Adding POSS-PEG to PLE, which is used as fibrous scaffolds, resulted in relatively smaller fiber diameter, narrower diameter distribution and improving initial cell attachment thanks to higher surface free energy of POSS siloxanes [44].

As a representative phospholipid 1,2-myristoyl-sn-glycero-3-phosphoethanolamine (DMPE) was chosen. Phosphatidylethanolamine (PE) is the second most prevalent phospholipid in humans located in the inner leaflet of the lipid bilayer and is the major phospholipid of bacterial membrane [45,46]. DMPE was used as a model lipid because, first, it is capable to form a range of phase states and undergoes characteristic phase transitions and, second, forms characteristic domains in the liquid expanded – liquid condensed phase transition region where its phase behavior can be modified by interactions with membrane active drugs or other lipids.

The present study focuses on exploring the molecular interaction between mixed system consisting of POSS-PEG compound and saturated phospholipid DMPE at the air/water interface. For this purpose, we combine the equilibrium isotherms experiments complemented with the information about molecule packing and orientation using surface potential sensor (SPOT), monolayer morphology obtained by Brewster Angle Microscopy (BAM) and the interfacial shear rheology (ISR). To establish the mutual miscibility the data obtained from the π-A isotherms were used to calculate the mean molecular area, the percent of interaction, the excess molecular area, the excess Gibbs free energy of mixing, compression modulus, interaction parameter, and activity coefficients. The parameters were quantitatively evaluated with the aim to understand the POSS-PEG - DMPE interaction better, which is of significance in potential biomedical applications, among others, as new functional materials or new drug delivery systems.

2. Experimental

2.1. Materials

1,2-myristoyl-sn-glycero-3-phosphoethanolamine (DMPE ≥ 99% pure) was purchased from Sigma-Aldrich. 3,7,14- tris{[ω-(hydroxy)(polyethoxy)propyl]di-methylsiloxy}-1,3,5,7,9,11, 14-heptaiso-butyltricyclo[7.3.3.15,11]heptasiloxan (POSS-PEG) was synthesized according to a procedure described elsewhere [47]. The chemical structures of both compounds are presented in Fig. 1. Solutions for the spreading were dissolved in chloroform of spectroscopic grade (Uvasol, Merck) in order to obtain the mixtures in different molar ratio of components at a final concentration of 1 mg/ml.

2.2. Methods

2.2.1. Isotherm experiment

All reported experiments have been carried out using a computer-controlled Langmuir balance (KSV Nima) equipped with a Langmuir